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Occurrence of antibiotics in rural catchments

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HIGHLIGHTS

- Among 23 antibiotics investigated, 15 occur in the mix hospital + domestic effluent.
- In rural watershed upstream of WWTP discharge, only fluoroquinolones occur.
- The discharge strongly impacts the river quality especially for the low flow period.
- Only fluoroquinolones are present in particulate phase in substantial quantity.
- Antibiotic distribution in the particulate phase controls their dissipation in river.

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ABSTRACT

The transfer of 23 antibiotics from domestic and hospital sources was investigated in two elementary river watersheds receiving wastewater treatment plant (WWTP) discharges, in relation with the hydrological cycle and seasonal conditions. Antibiotic concentrations in the effluent of a WWTP treating wastewaters from both hospital and domestic sources (18–12 850 ng L^{-1}) were far higher than those from domestic sources exclusively (3–550 ng L^{-1}). In rivers, upstream of the WWTP discharges, fluoroquinolones only were found at low concentrations ($\leq$10 ng L^{-1}). Their presence might be explained by transfer from contaminated agricultural fields located on the river banks. Immediately downstream of the WWTP discharge, antibiotic occurrence increased strongly with mean concentrations up to 1210 ng L^{-1} for ofloxacin and 100% detection frequencies for vancomycin, sulfamethoxazole, trimethoprim and three fluoroquinolones. Dilution processes during high-flow periods led to concentrations 14 times lower than during low-flow periods. Downstream of the discharge, the antibiotic dissipation rate from the water column was higher for fluoroquinolones, in relation with their high sorption upon suspended matter and sediment. Only five antibiotics (vancomycin and four fluoroquinolones ciprofloxacin, norfloxacin, ofloxacin and enoxacin) were partly distributed (11%–36%) in the particulate phase. Downstream of the discharge, antibiotic contents in sediment ranged from 1700 to 3500 ng g^{-1} dry weight, fluoroquinolones accounting for 97% of the total.

1. Introduction

Large amounts of antibiotics, from 100,000 to 200,000 t per year, are consumed throughout the world, in hospitals and at home, in veterinary use and aquaculture (Wise, 2002), and subsequent concerns have emerged during the last decade about the occurence of antibiotic residues (Rodriguez-Mozaz et al., 2015; Carraro et al., 2016). Also, in the 26 countries of the European Union, for 2012, 3400 t of antibiotics were sold for human use and 7982 t for food-producing animals (ECDC, 2015). In France, high consumptions of 760 t in human medicine and 1320 t in veterinary medicine were reported for 2005 (Moulin et al., 2008).

In human medicine, beta-lactams such as penicillins and cephalosporins make up the main class, accounting for 50%–70% of total antibiotic use (ECDC, 2010). In decreasing order, sulfonamides, macrolides and fluoroquinolones followed, their sum

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corresponding to about 15% of total use. In France, some antibiotics such as cefotaxime or vancomycin are strictly reserved for the hospital sector. In the veterinary sector, tetracyclines account for 40% of total consumption, followed by a combination of sulfonamides and diaminopyrimidines.

After administration, due to incomplete absorption or metabolization in target organisms, 10%–90% of the antibiotic dose may be excreted as metabolites (Kümmerer, 2009). The beta-lactam and fluoroquinolone compounds are mainly excreted (>70%) under unchanged form in urine (Marx et al., 2015), contrary to sulfamethoxazole, 80% of which being excreted as metabolites (Gill et al., 1997).

Antibiotics display a wide range of physicochemical properties which control their behaviour in the environment, and clear relationships were established between K_{ow}, K_{oc} and sorption to organic matter of soil or sediment (Tolls, 2001). Therefore, they are diversely eliminated by wastewater treatment plant (WWTP) processes and some of them remain ubiquitous in WWTP effluents (Rossmann et al., 2014). For norfloxacin, ciprofloxacin, erythromycin or sulfamethoxazole, classical treatments in municipal WWTPs display low removal efficiencies (Verlicchi et al., 2015). Therefore, large amounts of antibiotics might enter aquatic ecosystems directly via WWTP effluent discharge (Deblonde et al., 2011) or aquaculture activities (Sarmah et al., 2006). High concentrations of ciprofloxacin (10–80 ng L^{-1}) and norfloxacin (50–900 ng L^{-1}) were reported in surface water impacted by wastewater effluent in northern New Jersey (USA) (Gibs et al., 2013).

Many antibiotic residues have been found in surface water and sediment, sulfamethoxazole and trimethoprim being the most frequently detected at concentrations from 10 to 2000 ng L^{-1} (Hirsch et al., 1999; Kolpin et al., 2004; Kümmerer, 2009). Beta-lactams were very scarce because of their high tendency to undergo hydrolysis (Hirsch et al., 1999), while other antibiotics may persist up to several months as well in water (Ingerslev et al., 2001) as in sediment (Díaz-Cruz et al., 2003). In the Huangpu River (China), sulfonamides showed the highest concentrations in water, while tetracyclines and macrolides prevailed in sediment (Chen and Zhou, 2014), due to their strong sorption on organic matter (Yang and Carlson, 2003).

Consequently, antibiotic contamination might have deleterious impacts upon aquatic ecosystems and could favour the development of resistant bacterial strains, since WWTP discharges are hotspots for antibiotic release to water (Michael et al., 2013) and for antibiotic-resistance gene emergence (Rizzo et al., 2013). In the Seine River (France), a chronic high level of antibiotic-resistant *Escherichia coli* was reported, and the highest resistance levels were observed for tetracycline and amoxicillin/ticarcillin (Laroche et al., 2009).

In this context, the present study considered 23 antibiotics and two metabolites in WWTP discharge and surface water from two headwater streams in France, taking into account both the dissolved and the sorbed phases on suspended matter. These antibiotics were: sulfonamides - sulfamethazine (SMZ) and sulfamethoxazole (SMX); quinolones - oxolinic acid (OXO), nalidixic acid (NAL) and pipemidic acid (PIP); fluoroquinolones - flumequine (FLU), enrofloxacin (ENR), ciprofloxacin (CIP), ofloxacin (OFL), norfloxacin (NOR), enoxacin (ENO), lomefloxacin (LOM) and sarafloxacin (SAR); tetracyclines - tetracycline (TET) and chlortetracycline (CTE); macrolides - tylosin (TLS) and erythromycin (ERY); beta-lactams - amoxicillin (AMO) and cefotaxime (CEF); diaminopyrimidines - trimethoprim (TRI) and ormethoprim (ORM); nitro-imidazoles - ornidazole (ORN) and glycopeptides - vancomycin (VAN) and the two metabolites were *N*-sulfamethoxazole (*N*-SMX) and D-ciprofloxacin (D-CIP).

The main objective was to improve knowledge of transfer mechanisms in river water of antibiotics from domestic and hospital sources, in relation with the hydrological cycle and seasonal conditions. Two rivers were selected because of their small watershed areas (10.5 km^2 and 42 km^2) and a single WWTP effluent in each watershed. First, the occurrence and the distribution of antibiotics were investigated in the WWTP discharges. Then the occurrence and the fate of these chemicals were characterized over 1 year, including low- and high-water periods. Both the water column and the bed sediments which integrate contamination over the long term, were considered.

2. Material and methods

2.1. Description of study area

The study was conducted in two headwater tributaries (Strahler stream order: 1) of the Orge River watershed (a tributary of the Seine River, France): i) the Prédecelle River (basin surface area: 42 km^2) and ii) the Charmoise River (surface area: 10.5 km^2), both flowing through rural areas upstream of the small towns of Briis-sous-Forges and Fontenay-les-Briis (Essonne, France). The Prédecelle River flow ranged from 0.095 to 4.5 $m^3\ s^{-1}$ and that of the Charmoise River, from 0.005 to 0.2 $m^3\ s^{-1}$. The river flow was measured with an OTT current meter (Sheffield, UK) for each water collection.

These two small basins are equipped with separate sewer networks making it possible to follow the impact of the Briis-sous-Forges WWTP discharge that treats domestic wastewaters (100%) upon the Prédecelle River and of the Fontenay-les-Briis WWTP discharge that treats domestic (60%) and hospital (40%) wastewaters on the Charmoise River (Fig. 1). The sewage characteristics are presented in the Supplementary Material (Table SM. 1).

The Briis-sous-Forges WWTP built in 2009, operated with a combined decantation and biological treatment tank and then, nanofiltration through a membrane system retaining microorganisms and fine particles. The sludge was treated by lagooning through basins covered with reeds and rushes. The WWTP treated 950,000 m^3 of domestic wastewater yearly by biological processes and produced about 200 t of sludge. The treatment capacity corresponded to 20,000 inhabitant equivalents, while the population connected was 13000 inhabitant equivalents. Wastewater fluxes entering the WWTP ranged from 2170 to 3900 $m^3\ d^{-1}$ in 2010–2011.

The Fontenay-les-Briis WWTP built in 1979 and equipped with a combined tank (decantation and activated sludge), treated 157,000 m^3 yearly of a mix of domestic and hospital wastewaters by biological processes and produced about 32 t of dry sludge, all of which was spread upon agricultural land. The treatment capacity corresponded to 5000 inhabitant equivalents, while the population connected was 1715 inhabitant equivalents. Wastewater fluxes entering the WWTP ranged from 270 to 532 $m^3\ d^{-1}$ in 2010–2011.

2.2. Sampling schedule

From February 2010 to February 2011, six samples of WWTP effluent and surface water were collected by mean of stainless steel bottles, at two sites along the Prédecelle River: upstream (50 m) and downstream (15 m) from the WWTP discharge point (Fig. 1). The characteristics of the river samples are indicated in Table SM. 2.

Fourteen water samples of WWTP output and surface water, at three sites along the Charmoise River – upstream (50 m), downstream (15 m) and far downstream (950 m) from the WWTP discharge point – were collected monthly in 2010–2011; their characteristics are indicated in Table SM. 3. The sample collection at